

THE ANALYST.

JUNE, 1892.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

A meeting of the Society was held on Wednesday, the 4th of May, the President (Mr. Hehner) in the chair.

The minutes of the previous meeting were read and confirmed.

The following gentlemen were proposed as Members:—Mr. James William Westmorland, F.C.S., A.R.S.M., Analytical Chemist, 2, City Road, London, E.C.; Mr. Samuel Francis Barford, F.I.C., Member of the Pharmaceutical Society, Member of the Society of Arts, "Eastleigh," Queen's Road, Leicester; and Messrs. G. H. Gabb and W. N. Yarrow, assistants to Mr. A. W. Stokes, were proposed as Associates.

The following gentlemen were duly elected Members of the Society:—Percy Gerald Sanford, F.I.C., F.C.S., Analytical and Consulting Chemist, 20, Cullum Street, Fenchurch Street, E.C.; Mr. Harry Sylvester, F.I.C., F.C.S., Analytical Chemist, Holyhead Road, Handsworth, Birmingham; Mr. L. J. de Whalley, B.Sc. (London), Analytical Chemist; and Mr. Thos. Shortridge Tweedie was elected an Associate.

Mr. Harvey temporarily occupied the chair while the President read the following papers:—

NOTES ON BUTTER.

BY OTTO HEHNER,

IN the last number of THE ANALYST, reference is made to an observation which must have struck every analyst, namely, that whilst, as a rule, genuine butters when carefully melted, yield a fat which is practically clear, margarines and badly-adulterated samples melt very turbid.

I have for about a year past kept a record of most of the butter samples which have passed through my laboratory, and have noted the appearance on melting the samples in the water-oven, also the fact, whether preservatives were found or not, together with the result of the analysis.

370 samples have thus been examined with the following results :—

- 162 melted clear, and were genuine.
- 61 melted turbid, and were genuine.
- 81 melted turbid, and were adulterated.
- 66 melted clear, and were adulterated.

Of the 370 samples, 214 were preserved with borax or with boric acid, namely 119 genuine samples, or 53 per cent. of all genuine samples; and 95 adulterated ones, or 65 per cent. of all adulterated samples.

It is obvious from the above table, that while the majority of genuine samples, namely, 72·6 per cent., melted quite clear, and the majority, 55·1 per cent., of the margarines more or less turbid, nothing but the vaguest conclusions can be drawn from the appearance on melting. It is true, that in most cases in which the samples melted clear and yet were adulterated, the percentage of the admixture was comparatively small, say under 20 per cent. But I have met with adulterated samples containing 25, 30, 40, and even 94 per cent. of margarine, and yet they melted clear. These are isolated instances, but they remove the method quite out of the list of reliable ones.

I am not in a position to criticise the statements made by Drouot, Besana, and Wollny,* who all operated with a little apparatus devised by Drouot, whilst I simply melted my samples in a small beaker at the temperature of the water oven, but my results will be sufficient to make analysts cautious before placing reliance upon such a test.

The general use of boric preservatives should be noted.

NOTE ON THE LEFFMANN-BEAM METHOD OF DETERMINING FAT IN MILK.

BY OTTO HEHNER.

DRS. LEFFMANN AND BEAM have been kind enough to send me one of their centrifugal machines for the rapid estimation of fat in milk. I have made a few estimations of fat by means of this machine and give the results in the following table :—

	Fat by Coil.	Fat by Centrifugal.
1.	3·89	3·87
2.	2·51	2·54
3.	3·34	3·27
4.	3·32	3·27
5.	2·60	2·45
6.	1·85	1·76
7.	3·18	3·10

The results, as far as it is possible to judge from so limited a number of determinations, are therefore quite as accurate as claimed for them by the authors of the process. I find one minute's whirling quite sufficient to separate the whole of the fat. It is there-

* See abstract, ANALYST, vol. xvii., p. 100.

fore possible, by taking the specific gravity and the fat by the Leffmann-Beam process, to obtain an accurate milk analysis in a very few minutes, using Richmond's and my formula for the calculation of the total solids, or Richmond's slide rule.

I have not yet had time to investigate the exact *rationale* of the method, which is evidently not quite as simple as may at first appear. 15 c.c. of milk are taken, 3 c.c. of a mixture of equal parts of strong hydrochloric acid and of fusel oil are added, and then strong sulphuric acid up to the neck of the little bottle belonging to the machine. After careful mixing, so that all caseine has dissolved, hot dilute sulphuric acid is added up to the zero point of the graduation. Each division of the graduation corresponds to 0.15 c.c. or to 0.1 per cent. by volume of fat. The figure thus obtained is to be multiplied by 0.86; this is, however, not the specific gravity of the butter fat, which when read off is but little above its melting point. I presume the figure is one ascertained empirically, as the fat, after separation from the acid liquor beneath it, smells strongly of fusel oil, and is evidently not pure milk fat, but a mixture.

DISCUSSION.

Mr. Alfred H. Allen thought that the graduation of the tubes was based on the fact that 0.86 was approximately the gravity of milk fat at 100° centigrade, but with a substance with so high a co-efficient of expansion as butter fat, even a moderate alteration in the temperature would, he thought, materially affect the volume registered. He would like to know whether Mr. Hehner had made the experiment with water instead of milk, and if so whether any fusel oil had risen to the top of the liquid.

The President replied that he had not tried the experiment.

Mr. Allen, continuing, said that it was difficult to follow the reasoning which led to the adoption of an arbitrary process. The inventor began by taking 15 c.c. of milk; and then added a mixture of hydrochloric acid and fusel oil. He presumed the acid was used to obtain the fat in a kind of emulsion, and on then adding sulphuric acid the fusel oil was dissolved and the fat readily separated from the very dense liquid. It was also quite clear that any centrifugal apparatus would act better with two liquids of different densities, than if they possessed nearly the same density. The inventor could scarcely get very close or accurate results, unless he paid attention to the temperature at which he measured the fat, which could be very easily done by placing the tube in boiling water before observing the volume of the fat. The process described was an arbitrary process; but if it was really butter which came to the top, and not butter fat, *plus* fusel oil (which might be the case), it would be possible to confirm the result by the Werner-Schmidt process, and at the same time have a very useful preliminary indication of the amount of fat. In his opinion, the centrifugal plan ought to be capable of being very extensively applied for the separation of liquids, and had, in fact, been recently applied to that purpose by Mr. Thorner.

Mr. H. Droop Richmond pointed out that if the factor 0.86 was probably obtained by dividing 0.89, the density of butter fat at about 50° or 60° by 1.032 the density of

milk, the use of this factor would correct volume readings to weight percentages. He thought that the error caused by the contraction of the fat, owing to cooling, would be practically negligible and would fall within the unavoidable experimental error.

Mr. A. W. Stokes wished to ask whether the President had found that the fat rose by itself, because he (Mr. Stokes) had tried an experiment in a different sized glass, and he had found that casein rose from below and mixed with the fat, and the results were difficult to read off. Could the fat be read off accurately?

Mr. Woosnam wished to ask if Mr. Hehner had tried leaving the acid upon the milk for any length of time, to see if it had then any effect upon the percentage of butter fat; or whether, in order to get an accurate result, it was necessary to proceed at once with the "whirling" in the machine? Were there any black, solid particles left in the sulphuric acid mixture?

Mr. Hehner, in reply, said that he had not tried the experiment of leaving the acid in very long, because he had found from the few experiments made, that it was more satisfactory to perform the experiments at high temperature, and not to wait till the apparatus cooled down. In reply to the question asked by Mr. Stokes, he stated that if the experiment were properly done, there was absolutely no emulsion between the acid and the fat.

The President having resumed the chair, Mr. Allen read the following paper:—

ON THE PROPORTION OF WATER IN BUTTER.

By ALFRED H. ALLEN.

A good deal of interest is attached at present to the proportion of water which may be properly contained in butter, in consequence of the sudden appearance in the market of butters containing an unusually large percentage of water. In the years 1877 and 1878, the West Riding officials submitted to me several samples of butter which were found on analysis to contain large proportions of water. Thus I certified to 19·83, 22·24, and 25 per cent. respectively. Action was taken on my certificates and convictions obtained. Since that time, until quite recently, of the thousands of samples of butter which have passed through my hands, hardly any have contained a marked excess of water. It would scarcely have escaped notice in the ordinary process of preparing the butter-fat, and, in fact, the recent cases have forced themselves on my attention during the ordinary process of analysis, there being no previous suspicion that an abnormal proportion of water was present.

The first case among those of recent occurrence was that of a sample, said by the defence to be Cork butter, churned by small farmers from the produce of one or more cows each. On analysis, I certified it to contain 22 per cent. of water, the amount actually found being 22·44 per cent., and added that "In my opinion any proportion of water in excess of 16 per cent. as a maximum should be regarded as an adulteration." Without any evidence being adduced for the defence, it was submitted to Somerset House, when Messrs. Bell, Bannister and Lewin reported that "the sample of butter referred

to in the annexed letter was received here on the 9th inst. (December), securely sealed. We have analysed the butter and declare that it contains 22.98 per cent. of water. We are of opinion that such proportion of water is in excess to the extent, of at least 5 per cent." This certificate is eminently characteristic. It states the minimum adulteration without going further and saying what was the excess of water above the average proportion in butter. It is evident, also, that it fixes the Somerset House limit for water in butter at 18 per cent., and affords one more illustration of the perverse custom of the Somerset House Chemists of straining every point in favour of the defence, instead of occupying the more consistent position of impartial referees of the Court.

On page 64, *et seq.*, of his work on "Food," vol. ii., Dr. James Bell gives results of the analysis of 113 samples of butter, which he says were selected so as to obtain, as far as possible, fair representative samples of butter produced under different conditions; and in the *Report of the Board of Inland Revenue*, 1876, he states that "the samples may be taken as fairly representing the various qualities of butter as made and brought to market by farmers both in England and Ireland. Every care was exercised by the Board's local officers in procuring them, and there can be no question whatever as to their being genuine." I am afraid people who live in the rough world, outside the circle of Arcadian simplicity in which Dr. Bell apparently dwells, will be inclined to think that the Irish peasant-farmer is quite capable of taking, and even likely to take, a wicked delight in supplying an exciseman with an abnormal article. Dr. Bell's remarkable conclusion further presumes that no farmer introduces an excess of water into butter, or makes an addition of foreign fat. This assumption is strictly opposed to my own personal knowledge that margarine is, and has for years past, been habitually bought by dairy-farmers for incorporation in the butter subsequently made and brought to market. He further contends that butter not made for sale must necessarily be genuine, and so practically extends the definition of "genuine" to any butter which has passed through the hands of a careless or incompetent dairymaid, who thereby becomes the arbiter of quality. But Dr. Bell's more recent opinion, as laid down in his work on "Food," vol. ii., page 47, is that "*a greater amount of water in butter than 12 per cent. is unnecessary, so far as attaining a good appearance is concerned, and anything over 16 per cent. is injurious to the keeping qualities of the butter.*" Clearly, it was Dr. Bell's opinion at the time he published his second volume that 16 per cent. is the maximum limit of water to be allowed in butter, in which opinion I cordially concur, but in the modification of his opinion for the guidance of local magistrates, who expect to receive from him impartial advice, he fixes the limit at 18 per cent., and omits all mention of either the average or maximum proportion in well-made butter. This deplorable omission, which is consistent with the usual practice of the Somerset House Chemists, is of course, directly conducive to adulteration.

In the article on "Butter" contributed by Dr. Bell to Thorpe's *Dictionary of Applied Chemistry* (vol. ii., page 300), it is stated that "in commercial butters the water has been found to vary from 4 to about 18 per cent." Here, therefore, Dr. Bell abandons his

position that the exceptional butters included in his 113 commercial samples were "genuine," and again fixes his maximum for water at "about 18 per cent.," which may therefore be regarded as the present Somerset House limit.

There has lately been an organised and systematic attempt, emanating from certain German ports, to place heavily-watered butter on the English market, and hence public analysts should be on the look-out for samples of butter so sophisticated.

In my more recent certificates on watered butter, I have actually quoted Dr. Bell's words, giving him as an authority for the statement that "a greater amount of water than 12 per cent. is unnecessary, and anything over 16 per cent. injurious to the keeping qualities of the butter," and have stated my agreement with that opinion. Such a definite course as this is desirable in the face of the one-sided certificates issued by Somerset House, and of the fact that the solicitor for the defence in a recent case actually contended that *any* amount of water in butter was allowable, seeing that the Legislature had not defined the amount, "finding it impracticable to do so." Such assertions as these are usually made in the absence of the analyst, and if he becomes aware of them, it is only by accident and when the case is at an end; but it behoves public analysts to correct such flagrant misstatements of the scope and purpose of the Sale of Food and Drugs Act.

In 1875, the Society of Public Analysts proposed and adopted for butter the limit of 80 per cent. for butter-fat, leaving 20 per cent. for salt, curd and water. I think this is a perfectly proper limit, but it may be worth while to restate the fact, as I notice that at a recent convention of the American Association of Agricultural Chemists, the Society's limit was erroneously stated to be 85 per cent.*

In several cases since the one referred to Somerset House, I have met with upwards of 20 per cent. of water in butter, and proceedings have been taken and evictions obtained on my certificates. In one instance the proportion of water reached 29 per cent.!

In proceedings recently taken on my certificate for the sale of butter containing $21\frac{1}{2}$ per cent. of water, two inspectors from Cork Butter Market were witnesses for the defence. Their evidence was of so startling and novel a character that a short reference to it will not be out of place. They swore that they examined a very large number of samples daily; such a number that the testing of each must have been completed, if I remember their figures rightly, in a fraction of a minute. They observed the taste, smell, colour and consistency of the butter, and were inclined to dispute the analysis, on the ground that butter with so large a proportion of water would not have escaped their attention. They stated that the proportion of water met with in Irish butter sometimes reached 20 per cent; but it did not appear that they had ever actually ascertained the quantity or deputed an analyst to do it for them. They, however, swore that any abnormal proportion of water in the sample was probably due to the weather; for in wet weather the food of the cows was of course wetter, and hence the butter contained more

* To my astonishment, I find that the S. P. A. limit is incorrectly stated at 85 per cent., in vol. ii. of my "Commercial Organic Analysis."—A. H. A.

water! This novel and highly interesting statement was made in the witness-box. Further, they discriminated between "water in solution" and "water in suspension," but which of these curious forms was the normal, and which the abnormal constituent of the butter, was not made clear.

I find the proportion of water in butter to be most conveniently determined by placing five grammes of the sample in a small tared beaker, and exposing it in an air-bath, to a temperature not exceeding 110°C ., until no more globules of water can be observed on looking at the beaker from below. Generally, the water can be completely expelled in about one hour. The curd and salt can be subsequently determined in the same quantity. After evaporating the water, the fat is re-melted, and filtered into a small beaker kept in the water-oven. The residual matter is rinsed on to the filter with re-distilled petroleum spirit, and washed with petroleum spirit until free from fat. The filter is then dried at 100°C ., and the contents scraped off and weighed. After weighing, the residue, which represents the curd and salt of the butter, may be examined under the microscope for starch, cellular tissue, &c., and then, if desired, treated with cold water, and the solution further examined or titrated with standard silver solution to estimate the salt. Usually, however, it is sufficient to ignite the residue in porcelain at a low temperature, and regard the non-volatile matter as salt, the combustible as curd.

Some butters are far from being homogeneous, and when positive it is preferable to work on 25 or 50 grammes rather than on smaller quantities.

DISCUSSION.

The President remarked that lately, with the close competition in the butter trade, when 5% of margarine added to butter made mixing a profitable business, the attention of butter mixers had again been directed to the addition of water. As Mr. Allen had said, having regard to the systematic manner in which butter containing water was forced upon the market by unscrupulous dealers, every per cent. which such men could get recognised by the referees at Somerset House would be a very considerable gain to them and loss to the public. In his opinion, there was no reason why a butter should contain more than 13% of water. When the percentage of water rose above 15 it was either culpably added or negligently left in; and the excess was not only detrimental to the public but to the butter merchants themselves. He had been told by a merchant that, out of a consignment from a particular farmer, out of every hundredweight of butter he lost from 3 to 4 lbs. in transit; whilst, in ordinary butters, the loss was only from one-third to half-a-pound. On analysing a sample of the butter referred to, it was found to contain 18.8 per cent. of what the Irish Inspectors would call "undissolved water."

Mr. Cassal asked what method Mr. Allen used to estimate the water in butter? He wished to ask whether, on melting the samples of butter, the existence of any substantial adulteration with water was rendered evident? He understood Mr. Allen to say that this was so; and if so, it agreed with his own experience.

Mr. Stokes stated that he examined every sample of butter he received microscopically, and his experience was that if a butter contained an abnormal quantity of

water it could be easily seen. Some years ago it was a common occurrence to find large quantities of water in butter and lard; but of late they had not been nearly so frequent. Under the microscope it could readily be seen whether a sample contained margarine or whether it contained an abnormal amount of water.

Mr. Cassal wished to ask Mr. Stokes whether he relied entirely on the microscopic examination of his samples of butter for the purpose of deciding whether they could be passed or not?

Mr. Stokes replied in the affirmative.

Mr. Cassal would be glad, that being the case, if Mr. Stokes would give the Society full information as to the method of working. His own impression was that the method was quite unreliable. He would like to know if Mr. Stokes was able to distinguish between a sample of butter which contained from 10 to 12, and one which contained from 18 to 20 per cent. of water by microscopic examination. If so, the results attained were certainly remarkable.

Mr. Stokes expressed his readiness to read a paper before the Society on the subject.

Mr. Allen asked Mr. Stokes if he would at once explain to the Society the way in which he manipulated with the microscope in order to effect this desideratum.

Mr. Stokes replied that he took a butter, just as it came to him, and scraped a large surface clear. He then took a thin layer below this, and placed it on an ordinary microscope slide; over that he placed a microscopic cover-glass, and pressed this down, so that the butter formed a thin wedge. He now crossed the polarising prisms, so that the field of view was absolutely dark. On placing the slide between the prisms, if there was a trace of butterine or margarine, say within ten per cent., at once a glimpse of light came through. Badly constructed polariscopes let light pass without interposing an object, and are useless for this purpose. In the case of a genuine butter, there was no illumination at all. He had never once found this system fail. No selenite plate should be used, since its results are often delusive.

Mr. Allen replying generally to the remarks made, said that the test mentioned by Mr. Stokes had quite recently appeared in a trade journal, the only variation being that in that paper a plate of selenite was recommended, which he did not gather was the case with the method described by Mr. Stokes. Since that event, he had been asked by butter merchants if he was acquainted with the test. He had replied that he did know it, but that, in his opinion, it was only of value where large proportions of margarine were in question. In a paper recently published in America, it was proposed to dissolve the butter in a drop of oil, and examine it. Since the appearance of the article he had just referred to, he had tried the experiment, and he had found marked double refraction in genuine butters; and in the case of samples, which he believed to contain margarine in some cases he found double refraction, and in others, none. This caused him to come to the conclusion that there was more to be learnt before the process could be relied on. He would like to endorse what the President had said with regard to the undesirability of giving analytical data in the case of butter analyses. He contended that their clients

had absolutely no right to demand the figures on which they based their opinion as to the presence or absence of margarine; and he had, therefore, declined in recent instances to give them. He was told a few days before the meeting, that a letter written by a German house, contained the statement that "Mr. Allen was entirely behind the age; that he should use the Reichert test, and he would arrive at the same results as other, gentlemen." Seeing that he (Mr. Allen), had been among the first to adopt the Reichert distillation process, and recommended it to his brother chemists (ANALYST, x., 103; xii., 11; xiv., 5), and that at a period when the President (Mr. Hehner), doubted its value, even as a sorting test, this allegation was somewhat wide of the mark. But he held very strongly that an opinion on butter should not be based on the result of any single test. There were butters now in the market which were very skilfully adulterated, and it was only by the combined application of several tests that the fraud could be discovered; in fact, to his knowledge, it had escaped recognition in several instances of late. Analysts ought to be very careful not to give to their natural enemies, the adulterators, information respecting the methods they employed for the making of analyses. The discussions at the meetings of the Society were extremely valuable; but when it was known that THE ANALYST was bought regularly by all sorts of people, in order to see what could be done by analysts, and what could not be done, it was evidently extremely undesirable to let the general public know everything they were doing.

Mr. Cassal drew attention to the fact that a note had appeared in the *Times* on the adulteration of Normandy butter; and that it was pointed out therein that science failed entirely to detect certain percentages of margarine in butter, but that a test had now been devised, which was all that could be desired, and which "could be applied by an 'inspector' with the aid of a boy." He received Mr. Stokes' statement with all respect, and he would look forward with pleasure to the further information he had promised to lay before the Society. He, nevertheless, entertained considerable doubt as to the propriety of applying microscopic examination as the sole test for the passing of samples of butter.

A NEW AND RAPID METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC BODIES.

By W. F. KEATING STOCK, F.C.S., F.I.C.

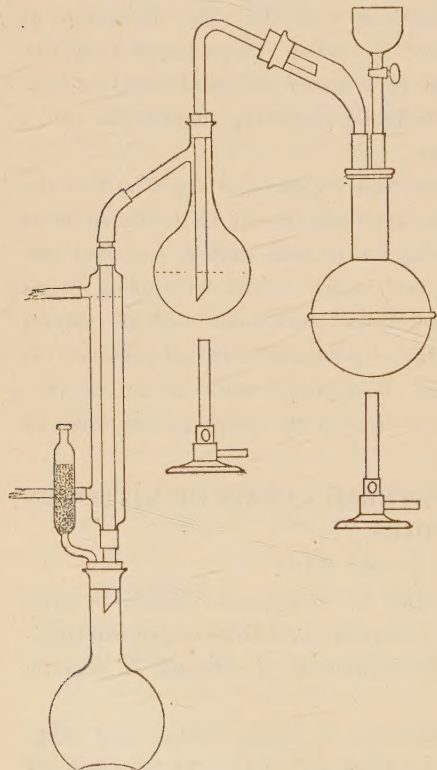
HAVING frequently been struck with the ready reduction of manganese dioxide in even slightly acid solutions, containing organic matter, it occurred to me to ascertain the possibility of turning this re-action to account, in the determination of nitrogen in organic combination.

Preliminary experiments proved that such substances as bones, cotton seed cake, linseed cake, fish flesh, pepper, and even coal and hard Durham coke, could be perfectly and rapidly oxidised by treatment with strong sulphuric acid and finely powdered manganese ore, at a temperature much below the boiling point of the acid.

It was also proved that the nitrogen of these bodies was thus converted into ammonia.

After a few trials with a "one to one" mixture of sulphuric acid and water, this was abandoned in favour of the strong acid, because it was found that the weaker acid led to a good deal of frothing. Eventually the process assumed a workable aspect, and stands as follows:—

From 0.5 to 1 gram of substance, according to the carbonaceous matter to be oxidised, is mixed in a conical flask or small beaker with 10 c.c. sulphuric acid of 1.84 specific gravity, and 5 grams of native manganese dioxide, which has been made to pass through a sieve with 36 holes to the linear inch. It is important that the oxide shall be fine enough, and yet not too fine. The flask is heated on an iron plate, until the contents assume a dark green colour, owing to the formation of manganic sulphate. This indicates the end of the re-action. The flask is cooled, cold water is added, and the contents transferred to an apparatus presently to be described. An excess of sodium hydrate in solution (20 grams for 10 c.c. sulphuric acid) is added, and the ammonia is distilled, collected, and titrated in the usual way.



The apparatus, which is shown in the accompanying figure, consists of a copper boiler of 600 c.c. capacity, closed by a screw cap and india-rubber washer. This cap carries a tapped funnel for the introduction of the sodium-hydrate solution, and a wide evolution tube to serve as a reflux tube, in case of sudden frothing. The evolution tube is closed by an I.R. stopper, carrying a tube bent at such an angle as will permit its passing down the centre of a Wurtz flask, which serves as a washing flask for the vapours from the copper boiler. Both boiler and flask are provided with burners, and both must be kept boiling throughout the experiment. The Wurtz flask is in turn connected with a 14-inch Liebig's condenser, set vertically, and this terminates in a 500 c.c. receiving flask, fitted with a guard tube filled with beads, through which the standard acid is run into the receiver. The open-ends of the tubes are all ground off at an acute angle, so as to prevent the formation of piston-drops.

Some remarks on the apparatus may not be out of place. I have adopted a copper boiler because, even when using the best bolt-heads I could procure, the fractures amounted to about 25 per cent., although zinc was used to lessen the bumping. With the copper boiler zinc is quite unnecessary, the boiling goes on in perfect quiet, and, so far as I see,

the copper flask does not suffer. The Wurtz flask, cannot, in my opinion, be dispensed with. I have tried every plan that would occur to an old campaigner to keep the sodium-hydrate back, but, without this intermediate flask, I have failed to get results to my satisfaction.

The method now disclosed cannot be looked upon as simply a modification of Kjeldahl's process. Kjeldahl effects oxidation at the expense of sulphuric acid; and although he uses potassium permanganate, to complete the oxidation, he does not rely upon it as a principal re-agent.

Kjeldahl's method requires much more time than the method I propose. I have completely oxidised a sample of bone powder in three minutes, and have determined the nitrogen in fifty minutes from the time of weighing out the sample.

I am making quantitative trials of the method as opportunity offers; new methods always require a little practice—I have compared it with the soda-lime combustion process on several samples of bone-dust, and the results from the two processes, whilst agreeing excellently among themselves, differ very little from each other.

The following will show what has been attained in the way of agreement:—

	Nitrogen by Combustion.		Nitrogen by New Method.	
Bone meal	...	3.54 per cent.	...	3.64 per cent.
Cotton cake	...	3.69 „	...	3.49 „
Fish flesh	...	7.41 „	...	7.51 „

It may be well to add a word of caution as to a source of loss of ammonia. Manures or other matters, containing a notable proportion of chlorides, could not be treated at once by this method. The chlorides must be decomposed by heating with sulphuric acid alone for twenty minutes, and the manganese dioxide can then be added at once, and this leads me to add that I have found a finely divided manganese dioxide, which has been given to me by my friend, Mr. John Pattinson, of Newcastle, as being a pure oxide, obtained by a "recovery process" on the large scale, to supply the place of Kjeldahl's permanganate, as used in his process, admirably, and to give infinitely less trouble.

It will occur to chemists that, in using this method, a "blank" experiment must be made with the re-agents, just as in Kjeldahl's process.

The following are further experimental results obtained by this method:—

By New Method.		FISH FLESH.	By Combustion.	
7.45	per cent. Nitrogen.		7.41	per cent. Nitrogen.
7.45	„ „			
7.47	„ „			
7.51	„ „			
7.45	„ „			
By New Method.		COTTON SEED CAKE.	By Combustion.	
3.61	per cent. Nitrogen.		3.68	per cent. Nitrogen.
3.49	„ „			

COMMERCIAL URIC ACID.

(Containing 99.3 per cent of uric acid)

Found.	Theoretically.
32.70 per cent. Nitrogen.	33.09
32.51 " "	

COMMERCIAL GELATIN (NELSON'S).

Two determinations gave 14.61 and 14.27 per cent. Nitrogen.

None of these determinations occupied more than one hour. Beakers of 180 c.c. capacity were used *for the oxidation*.

Attempts have been made to use the method for determining the nitrogen of ferrocyanides and some alkaloids, but so far without success.

DISCUSSION.

The President believed that the members of the Society would agree with him in thinking that any process which tended to simplify the determination of nitrogen—if experience showed that such method was so generally applicable as the Kjeldahl process was acknowledged to be—would be a valuable one to analysts.

Mr. Bernard Dyer wished, without criticising Mr. Stock's process, which he had not yet had an opportunity of trying, to take the opportunity of saying through the medium of *THE ANALYST*, that the use of permanganate in the Kjeldahl process—mentioned by Mr. Stock—was a decided mistake. It was not only quite unnecessary, but, in some cases, it might be a very serious source of error. Mr. Coste, and he, had made a number of experiments with the Kjeldahl process, with a view to testing the effect of the permanganate, and they had found that the use of it was very liable to occasion a loss of nitrogen. It was quite unnecessary, in the Kjeldahl process, to use permanganate at all. The best form of the Kjeldahl process was that in which sulphate of potash was used to raise the boiling point of the acid, and a drop of mercury added. In the figures which Mr. Stock had given, the use of manganese di-oxide did not appear to have produced any disastrous results; but he should advise anyone, before relying on it, to make experiments under various conditions, notably with known quantities of pure ammonia salts, bearing in mind the peculiar effect of permanganate in the kindred Kjeldahl process.

Mr. F. H. Perry Coste strongly endorsed Mr. Dyer's fears as to the danger of using manganese di-oxide. He considered that Mr. Stock had not proved his case, in spite of the closeness of the agreement between the results of the two processes. It would have been more satisfactory if he had made the check experiments by the usual Kjeldahl process. He wished also to point out that Mr. Stock had given very little information as to experiments with pure salts. In the only instance quoted (uric acid) the agreement was by no means close. Mr. Stock further stated that he entirely failed with ferrocyanide. This seemed to him a very important admission, seeing that the total nitrogen of ferrocyanide was readily obtainable by the Kjeldahl process.

Dr. Samuel Rideal pointed out that the addition of manganese di-oxide to the

sulphuric acid no doubt raised the boiling point, just in the same way as the addition of potassium sulphate did in the Kjeldahl process as worked by Mr. Dyer.

Mr. Coste stated that, by the use of potassium sulphate and mercury, one could complete the digestion in three-quarters of an hour, that being sufficient time for even such substances as gelatin.

Mr. Dyer explained that the essential difference between the two processes was that Mr. Stock did not boil, and so did not effect the oxidation at the expense of the acid.

Mr. Richmond's papers were deferred to the next meeting.

The Society's proceedings then terminated.

ON A RECENT CASE OF BUTTER ADULTERATION.

By CHARLES E. CASSAL.

Read at Meeting, April, 1892.

THE unsatisfactory state of things which may result under the present system of referring disputed cases of adulteration to Somerset House has been called attention to again and again. I greatly regret that it should fall to my lot to place one more instance on the long record of cases of difference between Public Analysts and the Chemists at Somerset House, for, were it possible, I think that it would be far preferable to deal with matters in dispute between us and those who are, after all, our professional colleagues, by methods other than those involved in public controversy. But I have no option in the matter; there is at present no other practical course open, and I hold that it would be wrong for a Public Analyst to submit tamely to the dismissal of cases undertaken on his certificates, because a Government Department sees fit to adopt singular and indeed *outré* views, and lest he should be taken as acquiescing in the maintenance of a system which is fundamentally bad, and which, in consequence, has often worked to the detriment of the analytical profession and to the injury of the public service.

In the month of December of last year a sample of butter was brought to me for analysis by an Inspector under the Acts. It had been purchased in a country district, within a short distance of the East coast. I certified that it contained at least 15 per cent. of foreign fat. I sent a portion of my sample to our President, Mr. Helmer, who certified it to contain 16 per cent. of foreign fat. The case was disputed, and the Inspector's reserve sample was sent to Somerset House. The certificate drawn up by the Chemists there, contained, as usual, and, as I hold, very improperly, statements of the percentages of water, "curd," salt, and fat—analytical details of no real bearing on the point at issue—and went on to state that "the result of a full analysis of the fat shows that the butter practically falls within the limits of the poorest quality of genuine butter met with in commerce, and they do not, in our opinion, afford evidence that foreign fat has been added to the butter."

With reference to the statements of the percentages of water, curd, salt, and fat, I may refer to a paper which I read at the February meeting of the Society, on "The

Drawing up of Certificates," in which the practice of the Somerset House Chemists in this respect was alluded to. I pointed out that these data have no bearing on the points at issue, and that their appearance in the certificates casts an unjustifiable reflection on the Public Analyst, implying, as it does, that these data should also appear in the certificate issued by him. The data relating to the analysis of the fat do not, however, appear in the Somerset House certificates.

I think that the Society will appreciate the reasons why I avoid mentioning analytical details in this case. I place the whole matter on this basis—that two Public Analysts, one of them the President of the Society of Public Analysts, and in addition to that fact, also one of the best known, if not the best known authority on the analysis of butter, have certified that a sample of butter was adulterated, practically to the same extent; and in view of the remarks I made on a previous occasion as to the undesirability in such cases as the present, of advertising analytical data, I do not think it well to publish them; but I will, of course, state them to the Society.

It will be observed that the wording of the Somerset House certificate is in some respects exceedingly cautious; but what it is that constitutes "poorness" of butter-fat is a question immediately raised by it. The term is inapplicable. It must, however, be held to mean that the fat departed to some extent in character from butter-fat, in the view of the Somerset House Chemists; and it plainly implies inferiority. From an analytical point of view, the fat of butter, or any fat, as such, can only justly be regarded as inferior in consequence of a difference in composition from that normally appertaining to the fat in question, such as would result from the presence of another fat; that is, *analytically*, inferiority of the *fat* of butter, if admitted, can only be constituted by the presence of another fat. I say, advisedly, inferiority of the *fat*. A butter may be poor; but I contend that in the present state of our knowledge it is not competent for anyone to talk of a "*poor*" butter-fat, except in the sense which I have indicated. A theory on this matter has been tentatively suggested to me; namely, that "poorness" in volatile fatty acids might constitute a "poor" butter-fat. If this were adopted as characterising a "poor" butter-fat, and if a butter-fat whose volatile fatty acids fall below a certain percentage is inferior in quality, then we have a possible definition; but until such a definition is made, and generally accepted, there is no such thing as "poor" butter-fat. It might properly be held that by the sale of a butter which was poor in volatile acids, and rich in fixed fatty acids, a purchaser was in no way injured, and that the butter was not in any sense inferior. It might even be looked upon as superior.

To Public Analysts the meaning of the Somerset House certificate is sufficiently obvious. I need hardly point out that it is on all accounts to be regretted that the Chemists who drew it up should differ from the great majority of Public Analysts in adopting indefensibly wide limits, and in showing so much leniency. The occurrence of cases of this kind is the more unfortunate as Somerset House is often erroneously looked upon as a sort of Court of Appeal. Some Magistrates have a habit, and a very bad habit it is, of taking the *dictum* of Somerset House as final. But it should be

pointed out that Magistrates are not only not compelled to adopt that *dictum*, but that it is undesirable that they should do so. They are bound only by the weight of the evidence that is before them. It would not be really difficult to show that the *dictum* to be relied on is that of the Council of the Society of Public Analysts, and not that of Somerset House. All matters of this sort should, in my opinion, be regulated by the Council of the Society of Public Analysts.

Somerset House may be regarded as a sort of Court for confirmation, which has again and again been proved to be quite mistaken; and once again in the present instance, for there is no reason to believe that there was any material difference between the Inspector's reserve sample and that analysed by Mr. Hehner and myself. The Court for confirmation, if it be one, is not to be looked upon as being abnormally free from the errors that beset mankind because it is a Government department, or on the strength of any other shibboleth. The Somerset House analysts are not necessarily more correct in their views and more certain in their results than any other analysts; I am, indeed, convinced that in their private capacities they would be the last persons to arrogate to themselves any such monopoly of knowledge and of accuracy. They have, at any rate, the distinction of being in an almost infinitesimal minority: but the fact remains that the Public Authorities concerned with the suppression of adulteration and the Public Analysts appointed by them are placed in a position of much difficulty in consequence of their undoubtedly conscientious, but mistaken action.

A discussion ensued in which the President, Dr. Alfred Hill, Dr. Vieth and others took part, and Mr. Cassal replied.

Volumetric Estimation of Sulphuric Acid in Sulphates. E. Stolle. (*Zeitsch. f. angew. Chem.* 1892, p. 234.)—Precht has modified Wildenstein's method by adding standard chromate in excess and titrating back the excess by means of a ferrous solution. The author further modifies the method by using a solution of barium chromate in the following manner:—A solution of barium chloride is precipitated hot with a slight excess of potassium chromate, a little barium chloride being finally added till the fluid is colourless. The precipitate is washed with hot water and is then dissolved in dilute hydrochloric acid.

The sulphate to be analysed is precipitated with a slight excess of this solution, ammonia is added, whereby the whole of the sulphuric acid is precipitated as sulphate, whilst a quantity of chromic acid, equivalent to the sulphuric acid which was present, is liberated and remains in the solution. This is filtered, and the chromic acid in the whole filtrate, or an aliquot portion of it, after acidification, is titrated with a standard ferrous solution. The results are very satisfactory and speedily obtained. Only one standard solution, that of the ferrous salt, is required. The author recommends an hydrochloric barium chromate solution of about 1.06 spec. gravity.

O. H.

On the determination of Phosphoric Anhydride in Thomas Slag. (*Staz Sper. Agr. Ital.* xix., 614; xx., 159; xxi. 225 and 453.)

The processes for attacking the slag are as follows:—

(1) With hydrochloric acid and potassium chlorate (three times the weight of the slag). (Olivieri.)

(2) With sulphuric acid (5 c.c. for each gram.), heating over naked flame until white fumes escape. (Loges.)

(3) With hydrochloric acid, 15 c.c. for each gram. of slag, evaporating to dryness to separate silica. (Konig-Martelli.)

(4) With aqua regia.

The solution is made up to a known bulk, and a quantity containing .1 — .2 grs. P_2O_5 is taken, 20 c.c. of a citric acid solution is added, and the solution nearly neutralized with 10 per cent. ammonia. After cooling 25 c.c. of magnesia mixture is added (a much larger quantity in the presence of much manganese. *Stutzer Land. Versuchst.*, 1890, 291), the mixture shaken till a precipitate begins to form, and $\frac{1}{3}$ of its bulk of 10 per cent. ammonia added. The precipitate is collected in the usual way and weighed as $Mg_2P_2O_7$ (Martelli, c. f. Konig, Martinotti and Olivieri.)

Mancusa-Limo adds to 2 grs. slag 25 c.c. dilute sulphuric acid (1 : 1), stirring well, and after two hours' repose adds warm water, filters and neutralizes with milk of lime; the liquid containing the precipitate, which darkens on exposure to the air, is heated on the water bath for half an hour, and then nitric acid is added till the precipitate is dissolved; the solution is cooled and filtered from silica, &c. The phosphoric acid is precipitated with molybdate, and converted into magnesium pyro-phosphate in the usual way.

The citrate method is inclined to give slightly high results, and the molybdate slightly low; with much manganese the latter is preferable.

H. D. R.

A Volumetric Method for the Estimation of Phosphoric Acid. By Matteo Spico. (*Gaz. Chim. Italiana*, xxii., i. 117.)—The author takes advantage of the fact that a solution of a phosphate added to a ferric solution produces a precipitate of ferric phosphate $FePO_4$, and the precipitation is complete, provided that complete neutrality is secured.

After obtaining his phosphate in solution (iron, aluminium, and manganese salts must be absent), he neutralises exactly with caustic alkali, using phenolphthalein as indicator; he then adds a small quantity of salicylic acid, and titrates with a solution of ferric ammonium alum (1 c.c. = .001 grm. P_2O_5 previously standardised on a solution containing 2.9439 grm. microcosmic salt per litre of which 1 c.c. also = .001 grm. P_2O_5) adding it in small quantities at a time, especially during the latter part of the titration; it is desirable to wait a little to let the white precipitated ferric phosphate settle down somewhat, as then the violet colour produced by the least excess of ferric solution is more easily seen.

The test experiments made with theoretical mixtures, minerals, and Thomas slag are very satisfactory, and the method agrees well with those of Olivieri, Mancuso, and Martinotti. (Compare preceding Abstract.)

H. D. R.

Observations on Butter Analysis. F. Jean. (*Revue Inter. d. Falsifications*, 1891, 65.)—A sample of pure butter forwarded by the Dutch chemists, Lobry de Bruyn and Van Leent, gave a R-W. figure of 20.75 and deviated to the left 20° of the author's oleo-refractometer.

The author suspected that the cow had been fed with linseed cake, which, according to Kildan's theory, should lower the soluble fatty acids; this theory is confirmed by Girard, who fed a cow with 2 kilo of linseed cake a day for 8 days, and then found 23.6 c.c. R-W. figure and -20° deviation in the oleo-refractometer. On increasing the amount of linseed cake to 4 kilos after 15 days he found 21.6 c.c. and -17° respectively.

He shows that high refracting adulterants (e.g., linseed oil), affect the oleo-refractometer reading much more than they do the Reichert-Wollny figure; thus a butter with a vegetable adulterant in small quantity gave 27.9 c.c. R-W. and -23° deviation, while with an animal fat he obtained 26.4 c.c. R-W. and -29° deviation.

The oleo-refractometer cannot decide in all cases whether a butter is genuine or adulterated, but it can be used to sort out samples as genuine, doubtful, and adulterated.

When a cow is fed on linseed cake (or, indeed, any other oil cake), the foreign fat passes into the butter.

Replying to the above, De Bruyn and Van Leent (*Revue Inter. d. Falsifications*, 1891, 78), admit the influence of linseed cake on the butters; it is largely used in Holland in the winter as an addition to hay. Their published analyses show that it has a much greater influence on the refractive index than on the volatile acids. They dispute the usefulness claimed by Jean for his oleo-refractometer even for sorting butters, because pure Dutch butters gave such discordant results.

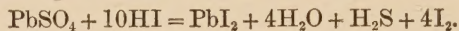
H. D. R.

On the Analysis of Galena and Lead Sulphate. R. Benedikt. (*Chem. Zeit.* 1892., xvi. 43, 44.)—The chief difficulty in the analysis of galena arises from the presence of gangue, from which the lead sulphate produced by the action of strong nitric acid and subsequent evaporation with sulphuric acid, has to be extracted either by repeated treatment with hydrochloric acid or with ammonium tartrate or acetate, or by digestion with sodium carbonate and subsequent solution in dilute nitric acid. The author has previously shown, in conjunction with M. Bamberger (*Monatshefte f. Chemie.*, 1891, xii. 1), that soluble sulphates, especially potassium sulphate, are easily converted into iodides by treatment with hydriodic acid, while barium sulphate is attacked more slowly. Free sulphuric acid is reduced to sulphuretted hydrogen. The method of analysis based on these facts is as follows: the sample is powdered finely enough to allow of a represen-

tative portion being taken, and a weighed quantity treated with a few c.c. of hydriodic acid of specific gravity 1·7, in a hemispherical porcelain dish. In order to avoid a too violent action it is best to cover the portion taken with a little water before adding the acid. After digesting for a short time on the water bath the contents of the basin is taken to dryness, allowed to cool, treated with dilute nitric acid, and again warmed, the lead being thus converted into nitrate, with separation of iodine.

The iodine is driven off by evaporation, the residue moistened with dilute nitric acid, the solution filtered, and the lead estimated in the filtrate by treatment with sulphuric acid in the usual way. A second digestion with hydriodic acid may be performed, but is rarely necessary. Test analyses, both on approximately pure lead sulphide, and on galena containing a good deal of gangue, as well as the sulphides of copper, zinc and antimony, gave satisfactory results.

In the case of lead sulphate the reaction is as follows:—



A considerable quantity of iodine is set free, and this, acting on the sulphuretted hydrogen, liberates sulphur, which is deposited on the walls of the beaker. Otherwise, the analysis proceeds as described above for galena.

The separation of sulphur may be avoided by covering the original substance before treatment with hydriodic acid, with water in which a small quantity of amorphous phosphorus is suspended, whereby the iodine is reconverted into hydriodic acid. A test analysis gave a satisfactory result. The author considers that the analyses of other sulphides may be facilitated by the use of hydriodic acid, and that the action of dilute nitric acid upon lead iodide may be taken advantage of in separating silver and lead. B. B.

The Rapid Determination of Free Sulphuric Acid in Aërated Waters.

P. Cazeneuve and Nicolle. (*J. Pharm. Chim.*, 1892, xxv. 51, through *Chem. Zeit.*).—Aërated waters often contain free sulphuric acid carried over mechanically from the generator. The amount is usually about 0·25 grams per litre, but occasionally is as much as double this. The process recommended by the author for its rapid detection and approximate estimation, depends upon the fact that calcium carbonate is precipitated when aërated waters are added to lime water, and dissolves in excess of the former, being reprecipitated on heating, and that should the aërated water contain a trace of free sulphuric acid this precipitate of calcium carbonate does not form, being converted into calcium sulphate, which remains in solution. The reagent used is lime water saturated at the ordinary temperature and free from any trace of alkali. One litre of water dissolves 1·29 grams of CaO at 15° C., 1 c.c. of the solution, therefore, corresponding to 0·0022 grams of sulphuric acid. 1 c.c. of the lime water is placed in each of five test tubes, and then 4 c.c., 8 c.c., 12 c.c., 16 c.c., and 20 c.c. of the aërated water to be tested added respectively. Should a turbidity appear in all the tubes on heating, the quantity of free sulphuric acid is negligibly small. Should, however, for example, the contents of the

third tube remain clear, while the second becomes turbid, the quantity of sulphuric acid necessary to neutralise 1 c.c. of lime-water is contained in something between 8 and 12 c.c. of the aerated water. The precise volume requisite can then be found by repeating the process with 9, 10 and 11 cc. of the aerated water. An obvious calculation gives the content of sulphuric acid per litre.

B. B.

The Examination of Wall Paper, Carpets, and Textile Goods for Arsenic, in Sweden. J. Landin. (*Chem. Zeit.*, 1892, xvi. 420.)—During the period from November, 1884, to the end of 1891, 9,632 analyses for arsenic in various textile materials and in paper hangings were carried out at the Kemiskt-tekniska Byran, in Stockholm, the main results of which are appended. The official method for the detection of arsenic prescribes that the arsenic shall be obtained as sulphide, and reduced by heating with potassium cyanide and sodium carbonate. If, when this is performed in a glass tube 1.5 to 2 mm. in internal diameter, a black or brownish-black mirror which is, at least in places, opaque, be formed, the following goods are condemned: Wall paper, roller blinds, artificial flowers, and similar articles coloured with water colours, when the test gives a positive result upon a quantity equal to 200 sq. cm. or less; all sorts of textile stuffs, yarn, lamp shades, sealing wax, wafers, stearin and other candles, when arsenic can be detected upon 100 sq. cm. or 21 grms., as the case may be. The method of examination is as follows: The article to be tested is distilled in a flask of about 300 c.c. capacity with 50 c.c. of hydrochloric acid of specific gravity 1.18-1.19, and 2 grms. of ferrous sulphate, both free from arsenic. In the case of so-called gold or bronze paint and other metallic articles, 2-3 grms. of ferric chloride are added. The distillate is received in 50 c.c. of water, and treated with 50 c.c. of a saturated solution of sulphuretted hydrogen. The precipitate of arsenious sulphide is collected on a filter 6-7 cm. in diameter, washed, and dissolved in dilute ammonia. The solution is evaporated to dryness after the addition of 0.02 grms. of sodium carbonate, and the residue is then heated in a bulb tube with 0.3 grms. of a mixture of dried sodium carbonate and potassium cyanide, in a stream of carbonic acid. The following are the numbers of the various articles examined:—

Wall papers	...	...	...	...	...	...	3,779
Textile goods	...	...	...	...	...	...	3,601
Carpets	...	...	...	...	...	...	1,084
Colours	...	...	...	...	...	...	305
Plush articles	...	...	...	...	...	...	227
Yarn	...	...	...	...	...	...	220
Thread	...	...	...	...	...	...	137
Linoleum	...	...	...	...	...	...	106
Miscellaneous	...	...	...	...	...	...	173

The following table shows the percentage that were found to contain arsenic, and of those the percentage which contained sufficient arsenic to yield an opaque mirror:—

				Containing arsenic.	Percentage of those containing much arsenic
Linoleum	...	...	...	59.4	38.1
Carpets	...	...	...	55.3	31.1
Wall papers	...	...	...	55.2	39.1
Plush	..	...	...	52.3	66.2
Yarn	...	...	...	45.0	44.4
Colours	...	...	...	43.3	74.4
Miscellaneous	...	...	...	41.4	75.3
Textiles	...	...	...	21.2	47.3
Thread	...	...	...	20.4	35.8
Average for the whole number	...	...	...	41.2	42.2

From these figures it appears that of the whole number of articles examined, 17.4 per cent. contained enough arsenic to lead to their condemnation. An improvement appears to be taking place, as the corresponding number for 1891 was 11.3 per cent. Of textile materials, those uniform in colour were freer from arsenic than those variegated in colour. Of brown fabrics 19.1 per cent. contained arsenic, while for other colours the figures were—red, 15.7 per cent.; green, 10.7 per cent.; blue, 10.6 per cent.; yellow, 6.8 per cent.; black, 3.0 per cent. White and grey fabrics were almost always free from arsenic.

B. B.

CORRESPONDENCE.

THE YEWS, REIGATE,

May, 18th, 1892.

GENTLEMEN,

To the Editors of THE ANALYST.

In a communication to the Society of Public Analysts, printed in your issue for the present month, Mr. Leo Taylor finds fault with me because I could not give an opinion as to the hygienic quality of certain samples of water from data furnished by his analysis. These data were "loss on ignition," "oxygen required to oxidise organic and other matter," and "organic ammonia."

I have elsewhere (*Jour. Chem. Soc.*, vol. xxi. p. 77, and vol. xxix. p. 825) stated very fully my reasons for rejecting these processes as indicators of organic impurity. It was only after I found that they condemned unpolluted mountain waters and did not convict impure shallow well waters, that I was compelled to abandon them. I came to this conclusion reluctantly, inasmuch as these processes can be carried out in a few hours, whilst the combustion process occupies several days.

Mr. Leo Taylor's analyses did not, as he alleges, include any estimation of "nitrogen as nitrates and nitrites," and therefore this trustworthy datum was not before me.

In conclusion, there can be no doubt that the rapid methods employed by Mr. Taylor find most favour with the great majority of chemists; but in cases of importance, such as the water supply of towns, recourse is almost always had to the combustion process.

I am, &c.,

E. FRANKLAND,